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Zinc Removal from Soil by Washing with Saponin Obtained from *Sapindus mukorossi*

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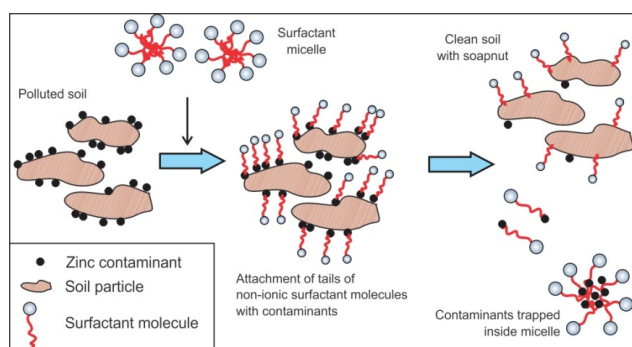
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Abstract

This study explores the possible application of a biodegradable plant-based surfactant saponin obtained from *Sapindus mukorossi* or soapnut, for washing zinc from contaminated soil. Batch experiments were conducted by varying pH, surfactant concentration and soil: solution ratio and compared to SDS, a synthetic surfactant. It was observed that soapnut was more efficient than SDS due to its lower pH. Also, the surfactants were more effective at higher concentrations. Soapnut solution removed more than 73% zinc while SDS solution could only wash out up to 31% of the total zinc from the soil under similar experimental conditions. pH played a very important role in zinc removal and at pH 4, both soapnut and SDS removed nearly similar amount of zinc. Analysis of the FT-IR data suggested that saponin did not interact chemically with zinc, offering an option for reusing the surfactant after precipitating the zinc by using NaOH at pH of 10.3. Damage to the soil was found to be negligible. This study concludes that soapnut can be used as a washing agent for removal of Zn from high iron soil with minimal damage to the soil.



Keywords: Soil washing; Soapnut; *Sapindus mukorossi*; Zinc; Plant based surfactant

Introduction

Soil is one of the most essential and non-renewable resources available to human beings. The socio-economic and environmental significance entitles soil for conservation and protection from all kinds of detrimental effects including pollution and erosion [1]. Among all the soil pollutants, the group of heavy metals contamination exists at more than 60% of the sites on the U.S. Environmental Protection Agency National Priority List and in 1,400,000 contaminated sites in Western Europe [2,3]. Among the heavy metals, zinc is one of the major soil contaminants. While natural concentration of Zn in soils

varies between 30 to 150 mg kg⁻¹, normal concentration of zinc in plant is usually 10-150 mg kg⁻¹. Plant toxicity is manifested at 400 ppm. WHO maximum permissible limit of zinc in drinking water is water is only 5 mg/L [4]. A European Union Council Directive has limited the values of zinc in arable soil to 300 mg kg⁻¹ for Zn [5]. According to a study in 2003, the annual worldwide release of zinc was 1,350,000 metric tons [6]. Zinc phytotoxicity has been demonstrated in soils contaminated by smelters and mining waste, incinerators, excessive applications of fertilizers and pesticides, burned rubber residues, galvanized materials, livestock manures and biosolid sewage sludge. Zinc tends to be accumulated to a greater extent in roots than in leaves, interfering with root growth and elongation, thereby limiting a plant's uptake of water and nutrients [7,8]. Excessive absorption of zinc on some adsorbent can suppress copper and iron absorption. The free zinc ion in solution

is toxic to bacteria, plants, invertebrates, and even vertebrate fish [9]. Although zinc is among the less toxic heavy metals, sheer volume of its release makes it a major soil pollutant in industrial sites.

Soil washing by natural surfactants is an important option for remediating contaminated soil [9]. A natural surfactant saponin can be obtained from the fruit pericarp of *Sapindus mukorossi* or soapnut. Soapnut tree is very common in Indo-Gangetic plains, Shivaliks and sub-Himalayan tracts at altitudes of 200-1500 m. The fruit pericarp of soapnut contains three types of triterpenoidal saponins viz oleanane, dammarane and tirucullane type [10]. Saponins available from soapnut have a number of uses as medicine and surfactants. In recent years, it has been used for washing soil contaminated with arsenic, heavy metals and organic pollutants [11-14]. In previous works, saponin from sources other than soapnut, was used to remove heavy metals such as Cd, Ni, Cu and Zn with up to 90% removal rate depending upon the type of soil and level of contamination [14-16].

In this study, the soil washing capability of saponin obtained from soapnut fruit for removing zinc has been investigated. Kinetics and mechanism of the Zn desorption process have been explored. Soapnut is compared with SDS, an anionic synthetic surfactant. Published research indicates the washing ability of commercial saponin [14-16]. However, in this work, saponin is directly extracted from soapnut, which obviates the need for commercial saponin purchase. Environment friendliness of the process has been examined by recovering zinc from the soapnut wash solution by precipitation and by evaluating the characteristics of washed soil.

Materials and Methods

Soil spiking and surfactant characterization

A composite soil sample was collected from the first layer aquifer in Hulu Langat area, Selangor, Malaysia. The soil was dried in an oven

overnight at 105°C following the procedure outlined by Roy et al. [11]. The soil was crushed and passed through 2 mm sieve, the particles larger than 2 mm sieve were rejected. The characteristics of soil are shown in Table 1. The soil was spiked with 1000 mg L⁻¹ solution of Zn(NO₃)₂ solution in the weight: volume ratio of 3:2 and stabilized for 4 weeks at room temperature. After 4 weeks, it was washed by artificial rain water following the method proposed by Oorts et al. [17-19] to increase the field relevance and thereafter equilibrated overnight. USEPA method 3050B was used to measure Zn content by ICP-OES and final Zn content of soil was found to be 540 mg Kg⁻¹. The XRD spectrum of the spiked soil revealed that the soil sample contained Silicon Dioxide as quartz (SiO₂, XRD displacement 0.158), Magnesium Aluminum Silicate Hydroxide as mica ((Mg,Al)₆ (Si,Al)₄O₁₀ (OH)₈, XRD displacement 0.119), Sylvine, sodian (C₁₁K_{0.9}Na_{0.1}, XRD displacement -0.171), Maghemite Q (Isometric Fe_{21.333}O₃₂, XRD displacement 0.001), feldspar Albite (Al NaO₈Si₃, XRD displacement -0.053). Zinc was not detected since it is absent in the mineral phase.

The natural saponin was extracted from the soapnut fruit pericarp by water and found to contain 65% saponin using UV-vis spectrophotometer. Based on some preliminary experiments, 0.5, 1, 1.5, 2 and 2.5% (w/v) soapnut solutions in water and 10, 20 and 30 mM SDS solutions (NaC₁₂H₂₅SO₄, C.P. grade, R and M Chemicals) in water were used for soil washing. The properties of the wash solutions are shown in Table 2.

Soil properties	Value	Method Soil particle size distribution
pH	4.5	USEPA SW-846 Method 9045D
Specific Gravity	2.64	ASTM D 854 - Water Pycnometer method
CEC (Meq)	5	Ammonium acetate method for acidic soil
Organic matter content	0.14%	Loss of weight on ignition
Bulk Density (gm cc ⁻¹)	2.348	
Total arsenic (mg kg ⁻¹)	3	Digestion by USEPA 3050B and measured by ICP-OES
Total iron (mg kg ⁻¹)	3719	
Total silicon (mg kg ⁻¹)	~390,000	
Total aluminium (mg kg ⁻¹)	2400	
Total manganese (mg kg ⁻¹)	185	
Total magnesium (mg kg ⁻¹)	635	
Total lead (mg kg ⁻¹)	11	
Total zinc (mg kg ⁻¹)	540	
Soil particle size distribution		

Sand (<50 µm)	92.66%	Sandy soil according to USDA Soil Classification
Silt (50-2 µm)	5.20%	
Clay (>2 µm)	2%	

Table 1: Characterization of spiked soil.

Extractants	Empirical Formula/ Chemical name	Mol Wt	Concentrations used	CMC at 25°C	Surface Tension (mNm ⁻¹)	pH
Soapnut (SN)	C ₅₂ H ₈₄ O ₂₁ .2H ₂ O	1081.24	0.50%	0.10%	41	4.63
			1%		40	4.44
			1.50%		39.5	4.35
SDS	NaC ₁₂ H ₂₅ SO ₄	288.38	10 mM	8.2mM	34	9.66
			20 mM		32	10.06
			30 mM		31	10.25

Batch experiments

Desorption of contaminants from soil was measured through batch experiments by shaking 1 gm of soil with different concentrations and volumes of surfactants in an orbital shaker following the procedure described by Jang et al. [20] with minor modifications. The experimental conditions and variables are mentioned in detail in Table 3. The suspensions were shaken and centrifuged at 4000 rpm for 10 min and the supernatant was withdrawn and filtered through a 0.45 µm nitrocellulose membrane filter, and subsequently stored by adding 1 drop HNO₃ acid. The filtrates from the experiments were analysed for zinc by ICP-OES using standard zinc solution (Perkin Elmer multi element standard). The experimental errors of ICP-OES were within the range of 2.461% to 2.983%.

Table 2: Surfactant characterization.

Effect of Surfactant concentrations	Standard conditions	– Soil/Solution ratio: wt:vol=1:20 (1 g soil : 20 mL solution)
		– Temperature=25°C
		– Shaking time 4 hrs
		– Unadjusted pH
	Variable conditions	– Soapnut (0.5%, 1%, 1.5%, 2%, 2.5%)
		– SDS (10 mM, 20 mM, 30 mM)
Effect of pH	Standard conditions	– Soil/Solution ratio: wt:vol=1:20 (1 g soil:20 mL solution)
		– Temperature=25°C
		– Shaking time 4 hrs
		– Surfactants=1% Soapnut and 20 mM SDS
	Variable conditions	– pH=4,5,6,7
Effect of Soil: Solution ratio	Standard conditions	– Temperature=25°C
		– Composition of aqueous solution:
		– Surfactants=1% Soapnut and 20 mM SDS
		– Shaking time 4 hrs
		– Unadjusted pH
	Variable conditions	Soil: Solution ratios: w/V=1:10, 1:20, 1:30

Table 3: Experimental conditions and variables.

Study of desorption kinetics

Kinetic study was conducted following methods of Tokunaga and Hakuta [21]. Desorption of contaminants from soil was performed by shaking 10 g of contaminated soil with 200 mL of two surfactants in an orbital shaker. Each lask was shaken at a speed of 135 rpm for up to 48 hours at 25°C. Samples of clay suspension of 5 mL volume were collected at intervals of 5, 10, 15, 20, 25, 30, 45, 60, 120 mins, 4, 6, 10, 15, 24, 48 hours. Every sample was double diluted, centrifuged at 4000 rpm for 10 mins, filtered through 0.45 µm nitrocellulose membrane filterand stored for ICP-OES analysis after adding 1 drop of HNO₃. In order to examine the zinc extraction mechanism, four mathematical models viz., two-constant rate, Elovich, parabolic diffusion and first-order kinetics equations were fitted to the kinetic data. By comparing the determination coefficients and standard errors of each model, the best fit model was determined [22-25].

Sequential extraction for soil fractionation: Tessier's procedure

Tessier's procedure has been applied to soils contaminated with various sources, such as irrigation with wastewater, mining activity, automobile emissions or sewage sludge addition (Figure 1) [26,27].

Recovery of wash effluent and damage to soil

NaOH solution was added with separate sections of wash effluent from zinc washing kinetic experiment (24 hrs washing) to maintain the pH between 9 and 11.5. Then the samples were filtered to separate the precipitated zinc and the concentration of zinc in solution was measured by ICP-OES. Some selected samples from batch experiments described in section 2.3 were analyzed for Ca, Mg, Si, Fe, Al to examine for any structural damage of soil following Zeng et al. [28].

Results and Discussion

Zinc removal by batch experiments

Figure 1a shows the removal of Zn from the soil by washing it with water, 20 mM SDS and 1% soapnut solutions at unadjusted pH. SDS has an alkaline pH in the range of 9-10, soapnut has acidic pH of 4.5 and water has neutral pH of 7 (Table 2). Water removed only 6% of the Zn, indicating that it bound strongly with the soil. Although SDS is anionic and soapnut is non-ionic, the efficiency of soapnut solution is higher than anionic SDS indicating that reduction of surface tension between soil particles and wash liquid interface, micellar solubilisation and lower pH played a more significant role than ionic interactions. The mobility of Zn depends largely upon pH, much higher in the range 4-6, decreasing significantly above 6 [29]. While soapnut solution of 1% concentration removed 68.33% Zn, 20 mM of SDS solution could remove only 30.11% of the Zn from soil. Figure 1b shows Zn removal by SDS and soapnut at different concentrations and at fixed soil solution ratio of 1:20. It was observed that the Zn extraction increased with increasing surfactant concentrations. Soapnut at 0.5% concentration removed 66.43% zinc and the removal increased to 73.54% at 2.5% concentration. However, 1% concentration of soapnut removed 72.33% of zinc and 2.5% concentration did not improve the performance much. SDS removed less zinc than soapnut. At 10 mM, SDS removed 22.66% zinc and 30 mM removed 31.45% of zinc. At higher concentration of surfactants, the solution contains more micelle and has lower surface tension that helps in solubilising the contaminant more effectively. pH is one of the most important factors

in removing heavy metals since it has a strong bearing on the solubility of metals in aqueous media. At lower pH, higher concentrations of H⁺ ions compete with the contaminants for the adsorption sites. In order to determine the effect of pH on the desorption efficiencies of Zn(II) ions, pH was varied between 4 to 7 using HNO₃ and NaOH. It was observed earlier that soapnut did not undergo any structural change with change in pH [30]. Also, it is not feasible to remove metals at pH higher than 7 due to reduced solubility [16].

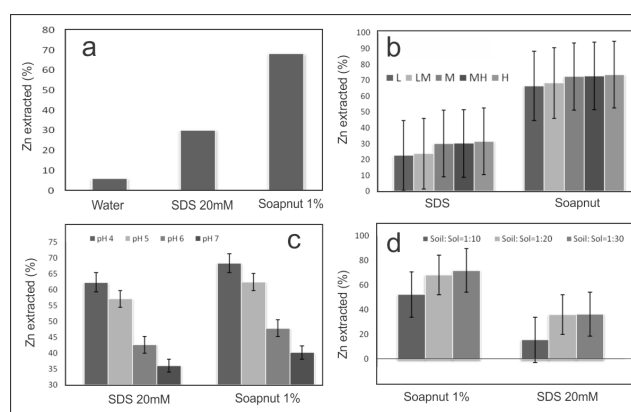


Figure 1: (a) Zinc extraction with water, 20 mM SDS and 1% soapnut solutions at unadjusted pH; (b) Effect of surfactant concentration on Zn removal at soil: solution ratio of 1:20 (SDS: L=10 mM, LM=15 mM, M=20 mM, MH=25 mM, H=30 mM; Soapnut: L=0.5%, LM=1%, M=1.5%, MH=2%, H=2.5%);(c) Zn removal by SDS and soapnut at different pH values at soil: solution ratio of 1:20; (d) Effect of soil: solution ratio on Zn removal at pH 5.

The effect of pH on the removal of heavy metals from soils is shown in Figure 1c. It is observed that best Zn removal efficiency was obtained at pH of 4, viz. 62.35% by 20 mM SDS and 68.33% by 1% soapnut. As the pH was increased, the removal became significantly less. At pH 7, SDS and soapnut removed only 36 and 40% Zn respectively. These observations match with the results obtained by other researchers who obtained almost 90% Zn removal by saponin at pH of 3 and around 20% removal at pH of 7 [16]. However, such low pH as 3 will not be beneficial for soil environment. So, intermediate pH such as 4-5 may be used for practical purposes. Figure 1d shows the results of zinc desorption at three different soil mass (gm) to extractant volume (mL) ratios for contaminated soil sample. For both 1% soapnut and 20 mM SDS, zinc desorption increases with an increase in the soil: solution ratio. Zinc desorption with 1:10 ratio of 20 mM SDS is extremely low at 15.55%. It increases considerably at 1:20 ratio to 36.12%, and then remains almost unchanged at 1:30 ratio under unadjusted pH. It is envisaged that 1:20 ratio had the advantage of presence of more micelles than 1:10, but the 1:30 ratio had the disadvantage of increasing pH that eventually balanced the advantage of having even greater number of micelles compared to 1:20 ratio. Again, for soapnut, the increase from 1:10 to 1:20 was significant, but the increase from 1:20 to 1:30 was about 3% only. So, the ratio of 1:20 may be suitable for soil washing purpose.

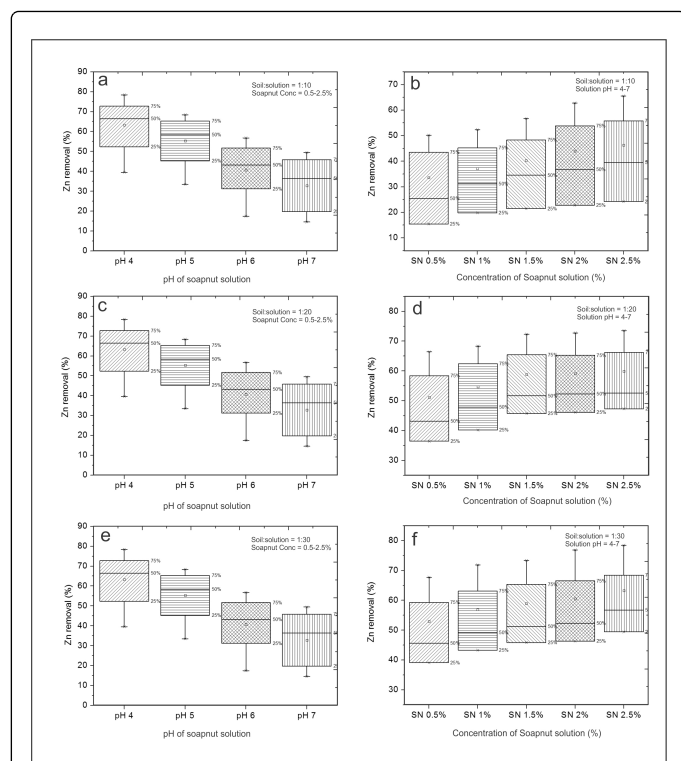


Figure 2: Variation in heavy metal removal at different saponin concentrations and different pH values: (a) and (b) soil:solution ratio of 1:10, (c) and (d) soil:solution ratio of 1:20, (e) and (f) soil:solution ratio of 1:30. The Box-whisker plot represents maximum score, 75th percentile (Upper Quartile), Median, 25th percentile (Lower Quartile), Median, 25th percentile (Upper Quartile) and Minimum Score.

A box plot has been shown in Figure 2 which has been plotted by varying soapnut solution pH from 4 to 7, soapnut concentration from 0.5 to 2.5% under different soil:solution ratios of 1:10, 1:20 and 1:30. The box-plot corroborates the data presented in Figure 2 and investigates the relative importance of different factors on Zn removal. It shows that for all the soil:solution ratios, the soil washings were most effective at lower pH around 4, which is also the natural pH of soapnut solution. As evident from Figures 2a, 2c and 2e, the zinc removal decreased with increasing soapnut solution with pH 4 to 7. Figures 2b, 2d and 2f show the increase in zinc removal with increase in soapnut concentrations. However, the improvement in performance is not very pronounced as that of pH. Also, the soil: solution ratio did not have a very large impact on the zinc removal and stayed almost same for 1:20 and 1:30. So, the boxplot reveals that pH is the most important factor in washing Zn from soil, followed by surfactant concentration and soil: solution ratio.

Desorption kinetics of Zn

The experimental result of Zn desorption kinetics is shown in Figure 3, where the concentration of Zn in the wash solution at different times has been plotted against time for soapnut and SDS. Although experiments were continued for 48 hours, the figures show results up to 6 hours and equilibrium was attained within 4 hours. There was a slight plateau region during the time period of 20-40 mins, after which

desorption increased once again to get stabilized at 4 hours. In order to achieve maximum desorption and investigate the corrosive effect of soapnut on the soil, we used 4-hour period for all other experiments. All the extractants attained equilibrium by the same time. The decreasing order of amount of zinc desorbed in 4 hours was soapnut 2% > soapnut 1% > SDS 20 mM. The curves have been fitted to logarithmic equations and the R^2 values are above 0.90, as shown in the Figure 3.

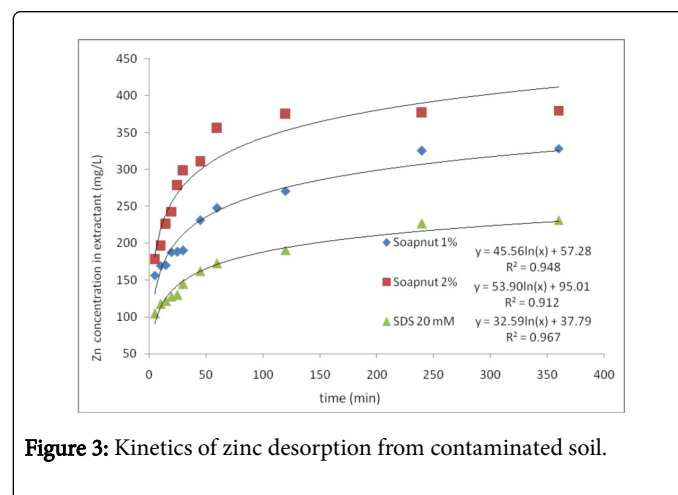


Figure 3: Kinetics of zinc desorption from contaminated soil.

The linear forms of the kinetic models, parameters, desorption rate constants, correlation coefficients (R^2) and standard errors (SE) of these models were measured. A higher value of R^2 and a lower value of SE indicate a better representation of the model. The desorption kinetic data for 1% soapnut and 20 mM SDS are fitted into four models to determine the best fit. When means of R^2 and SE are calculated for all the models, the two-constant rate equation is obtained as the best fit with higher R^2 and lowest SE values of 0.958 and 0.017 respectively. For both soapnut and SDS solutions, Zn was released at a faster rate during the initial 100 min, after which it slowed down. This differed from Hong et al. [16] who observed that Zn desorption by saponin from clay loam, loam and sandy clay loam soils followed first order kinetics.

Zeta potential and FT-IR spectral data

The zeta potential values of the fine soil particles were measured in de-ionized water, 20 mM SDS and 1% soapnut solutions and were found to have values of -34.3 ± 0.3 , -61.8 ± 0.2 and -11.8 ± 0.6 mV respectively. Therefore, in the case of both SDS and soapnut, zeta potential values underwent significant change. As compared with water, the zeta potential decreased significantly for 20 mM SDS, which indicates adsorption of the anionic surfactant SDS on the surface of soil particles. A similar decrease in zeta potential of kaolinite was observed when it sorbed SDS on its already negative basal plane, because of the original negative kaolinite charge plus the negative charge due to sorbed SDS headgroups [31]. However, the zeta potential value was much higher for soapnut due to the non-ionic tails of saponin molecules, which were adsorbed on the soil particles, thereby reflecting higher zeta potential values. It was postulated that surfactant adsorption is essential for the removal of soil contaminants, and surfactants that adsorb at the soil-water inter-phases are better detergents [32]. Therefore, soapnut and SDS, both were adsorbed on soil particle and were effective detergents. Figure shows the differences in average absorbance spectra for the original soapnut solution and the

wash solution containing Zn. The absorption range of different molecular vibrations present in phenolic-OH, carboxylic acids and alkene groups are evident in both the spectra. No significant shift of peak or structural alteration can be found in the soapnut solution when it came into contact with zinc in the soil. So, it can be concluded from Figure 4 that no chemical interaction involving bond breaking and bond making is involved in the zinc removal by soapnut solution, although Hong et al. [16] proposed formation of metal-saponin complex. Similar analysis in UV-vis frequency range also didn't show any shift in the peaks (data not shown).

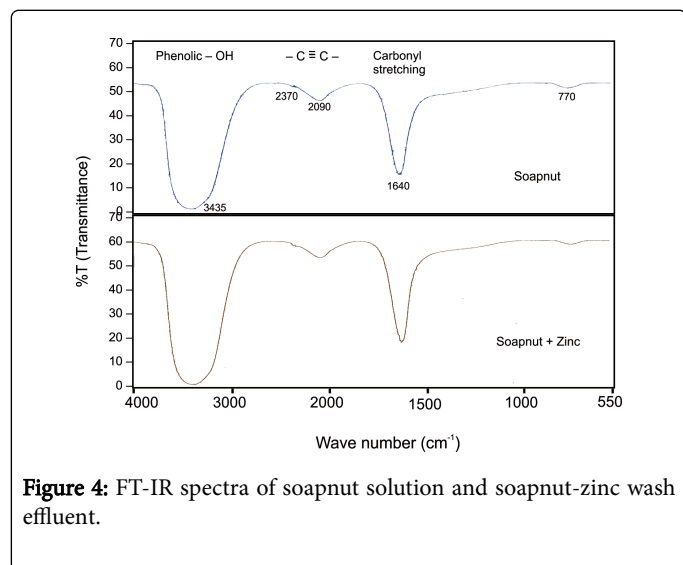


Figure 4: FT-IR spectra of soapnut solution and soapnut-zinc wash effluent.

Sequential extraction of zinc

Zinc (+2) in the soil before and after desorption, was fractionated by the sequential extraction procedure established by Tessier et al. [27]. The results are shown in Figure 5.

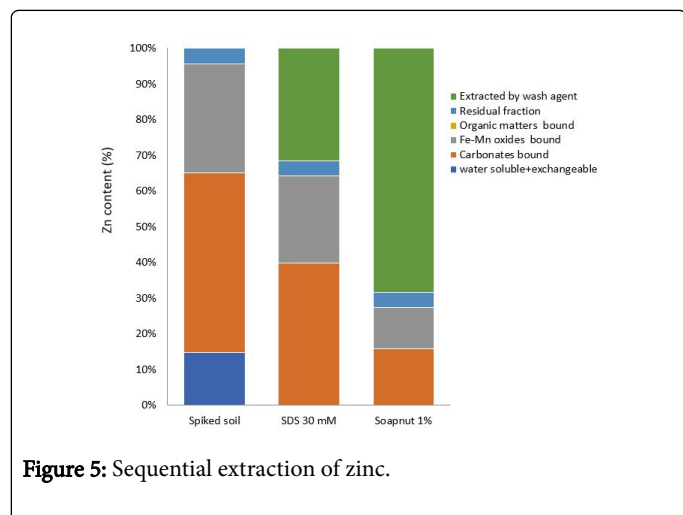


Figure 5: Sequential extraction of zinc.

In the spiked Zn contaminated soil having chemical composition as described in Table 1, Zn is retained mainly in Fe-Mn oxide bound fraction (30.66%), carbonate bound fraction (50.34%) and water soluble+ exchangeable fractions (14.73%). Organic fraction was negligible in the original soil, so Zn bound with this fraction is absent. Residual fraction has only 4.27% Zn. The water soluble and

exchangeable fraction is the easiest to remove and all the extractants removed almost all of the Zn in this fraction. SDS of 30 mM concentration could remove up to 31.45% total Zn from the soil. Among this, 14.73% was exchangeable fraction, 10.52% was carbonate bound fraction and 6.20% was Fe-Mn bound fraction. By using 1% soapnut solution, a total of 68.33% Zn could be removed from the soil. Among this, 14.73% was exchangeable fraction, 34.48% was from carbonate fraction and 19.12% from Fe-Mn oxide bound fraction. This indicates that the extractants that tend to remove Zn from carbonate and Fe-Mn oxide bound states are more successful. Soapnut was able to remove Zn from these two fractions more than SDS. Hence soapnut is better agent for soil washing.

Treatment of wash effluent

A conventional way of removing heavy metals from a solution is by precipitation under alkaline pH as hydroxides, carbonates, sulphide salts of the metals [16,33]. Therefore, precipitation method was used to separate the solubilised Zn from soapnut wash liquid. The wash effluent from the kinetic studies was used for this purpose. Table 4 shows the precipitation of heavy metals from wash effluents by adding NaOH. On addition of NaOH on soapnut, the precipitation process was completed when the pH reached 10.5. The hydroxide salt of Zn has solubility of only about 0.2 mg/L at pH 10.3, after which, it begins to increase. The amount of metal precipitation increased as the pH was increased to 10.3 when almost 94% Zn in soapnut effluent precipitated. However, on further increase in pH to 11, the hydroxide of Zn started to dissolve and only 42% Zn remained in precipitate form. The precipitate of zinc hydroxides at pH 10-10.3 can be then separated by decantation and filtration.

pH	Zn removal by NaOH	
	mg/L	%
9	262.46	69.07
9.5	296.22	77.95
10	334.65	88.07
10.3	356.54	93.83
11	160	42.11
11.5	90	23.68
Initial Zn concentration in wash solution=380 mg/L		

Table 4: Zinc removal from soapnut wash effluent.

Damage to soil

Dissolution of soil mineral components such as Ca, Mg, Al, Si and Fe on washing with soapnut and SDS solution was evaluated (Table 5). In this case, no considerable degradation was found in the soil structure. Both extractants dissolve very low percentage of these metals indicating negligible chemical weathering. High amount of Mg, Ca and Fe were present in the soil as observed from the XRD spectra. Therefore, their percentage in the extractants was higher than Al and Si which were bound more strongly as a part of the mineral structure of the soil. The extractants were not strong enough to dissolve Al and Si. It may be concluded that the soil washing by soapnut is safe for soil environment.

Extractant	Concentration	Dissolution of metal from soil (% of total content)				
		Ca	Mg	Fe	Al	Si
Soapnut	1.50%	1.97	2.05	0.42	0.46	0
SDS	30 mM	0.33	1.02	0.14	0.18	0

Table 5: Metal dissolution from washed soil.

Conclusion

Soapnut solution was effective in removing Zn from contaminated soil. SDS was less effective than soapnut. Since soapnut is non-ionic [34-36], ionic interaction did not take part in the desorption process. Lower pH of soapnut helped it in removing more zinc than SDS. Removal of zinc increased with surfactant concentration and lower pH of wash solution. The zinc desorption kinetics followed two-constant rate equation. The rate of desorption of zinc was quite fast during the first 100 mins after which it slowed down. Although it was previously thought that saponin formed some complex with heavy metals [16,37], no proof of such complexation is found in FT-IR spectra. Micellar solubilisation is found to be the principal zinc removal mechanism as established by zeta potential measurement. The soapnut wash solution can be reused after precipitating the zinc by using NaOH to maintain the pH at 10.3 when 94% of the dissolved zinc precipitated. Finally, it can be stated that while material cost for washing 1 ton of soil by 1% soapnut will be USD 28.57, washing by 20 mM SDS solution will cost about USD 27.7, going by the present market rate. Material handling, structural installation and operational cost being similar, both the natural and synthetic surfactants have comparable cost factors, with the added advantage of environmentally safe and biodegradability in favour of soapnut. Soapnut, being non-toxic to the living organisms and having natural origin, will have no detrimental effect on soil environment [29,38-40].

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References

- European Commission (2013) Soil Environmrnt.
- ETCS (1998) Topic report: Contaminated sites. European Topic Centre Soil, European Environment Agency, Copenhagen, Denmark.
- USEPA (1992) Considerations in groundwater remediation at superfund sites and RCRA facilities-update, Directive 9283.1-06 In: U.S. Environmental Protection Agency OoSWaER (ed), Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, USA.
- Lenntech (2004) Water Treatment and Air Purification.
- Grčman H, Velikonja-Bolta Š, Vodnik D, Kos B, Leštan D (2001) EDTA enhanced heavy metal phytoextraction: metal accumulation, leaching and toxicity. Plant and Soil 235: 105-114.
- Singh OV, Labana S, Pandey G, Budhiraja R, Jain RK (2003) Phytoremediation: an overview of metallic ion decontamination from soil. Appl Microbiol Biotechnol 61: 405-412.
- Castiglione S, Franchin C, Fossati T, Lingua G, Torrigiani P, et al. (2007) High zinc concentrations reduce rooting capacity and alter metallothionein gene expression in white poplar (*Populus alba* L. cv. Villafranca). Chemosphere 67: 1117-1126.
- Disante KB, Fuentes D, Cortina J (2010) Sensitivity to zinc of Mediterranean woody species important for restoration. Science of the Total Environment 408: 2216-2225.
- Fosmire GJ (1990) Zinc toxicity. The American Journal of Clinical Nutrition 51: 225-227.
- Suhagia BN, Rathod IS, Sindhu S (2011) Sapindus Mukorossi (Areetha): An Overview. International Journal of Pharmaceutical Sciences and Research 2: 1905-1913.
- Kommalapati RR, Valsaraj KT, Constant WD, Roy D (1997) Aqueous solubility enhancement and desorption of hexachlorobenzene from soil using a plant-based surfactant. Water Research 31: 2161-2170.
- Mukhopadhyay S, Hashim MA, Allen M, Sen Gupta B (2013) Arsenic removal from soil with high iron content using a natural surfactant and phosphate. Int J Environ Sci Technol, pp: 1-16.
- Mukhopadhyay S, Mukherjee S, Hashim MA, Sen Gupta B (2015) Application of colloidal gas aphron suspensions produced from Sapindus mukorossi for arsenic removal from contaminated soil. Chemosphere 119: 355-362.
- Song S, Zhu L, Zhou W (2008) Simultaneous removal of phenanthrene and cadmium from contaminated soils by saponin, a plant-derived biosurfactant. Environmental Pollution 156: 1368-1370.
- Gusiatin ZM, Klimiuk E (2012) Metal (Cu, Cd and Zn) removal and stabilization during multiple soil washing by saponin. Chemosphere 86: 383-391.
- Hong KJ, Tokunaga S, Kajiuchi T (2002) Evaluation of remediation process with plant-derived biosurfactant for recovery of heavy metals from contaminated soils. Chemosphere 49: 379-387.
- Oorts K, Ghesquiere U, Smolders E (2007) Leaching and aging decrease nickel toxicity to soil microbial processes in soils freshly spiked with nickel chloride. Environmental Toxicology and Chemistry 26: 1130-1138.
- Minase NA, Masafu MM, Geda AE, Wolde AT (1965) Heavy Metals in Agricultural Soils of Central Ethiopia: The Contribution of Land Use Types and Organic Sources to Their Variability. Open Journal of Soil Science 6: 891-901.
- Storer DA (1984) A simple high sample volume ashing procedure for determining soil organic matter. Commun Soil Sci Plant Anal 15: 759-772.
- Jang M, Hwang JS, Choi SI, Park JK (2005) Remediation of arsenic-contaminated soils and washing effluents. Chemosphere 60: 344-354.
- Tokunaga S, Hakuta T (2002) Acid washing and stabilization of an artificial arsenic-contaminated soil. Chemosphere 46: 31-38.
- Backes CA, McLaren RG, Rate AW, Swift RS (1995) Kinetics of cadmium and cobalt desorption from iron and manganese oxides. Soil Science Society of America Journal 59: 778-785.
- Carski TH, Sparks DL (1987) Differentiation of soil nitrogen fractions using a kinetic approach. Soil Science Society of America Journal 51: 314-317.
- Chien SH, Clayton WR (1980) Application of Elovich equation to the kinetics of phosphate release and sorption in soils. Soil Science Society of America Journal 44: 265-268.
- Evans RL, Jurinak JJ (1976) Kinetics of phosphate release from a desert soil. Soil Science 121: 1205-1208.
- Agnieszka J, Barbara G (2012) Chromium, nickel and vanadium mobility in soils derived from fluvioglacial sands. Journal of Hazardous Materials 238: 315-322.
- Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry 51: 844-851.
- Zeng M, Liao B, Lei M, Zhang Y, Zeng Q, et al. (2008) Arsenic removal from contaminated soil using phosphoric acid and phosphate. Journal of Environmental Sciences 20: 75-79.

29. Warwick P, Hall A, Pashley V, Van der Lee J, Maes A (1998) Zinc and cadmium mobility in sand: effects of pH, speciation, Cation Exchange Capacity (CEC), humic acid and metal ions. Chemosphere 36: 2283-2290.
30. Roy D, Kommalapati RR, Mandava S, Valsaraj KT, Constant WD (1997) Soil washing potential of a natural surfactant. Environ Sci Technol 31: 670-675.
31. Ko SO, Schlautman MA, Carraway ER (1998) Effects of Solution Chemistry on the Partitioning of Phenanthrene to Sorbed Surfactants. Environmental Science and Technology 32: 3542-3548.
32. Raatz S, Härtel G (1996) Application of surfactant combinations for cleaning clays contaminated with polycyclic aromatic hydrocarbons. Anwendung Von Tensidkombinationen Zur Reinigung PAK-kontaminierter Tone 37: 57-62.
33. Di Palma L, Ferrantelli P, Merli C, Biancifiori F (2003) Recovery of EDTA and metal precipitation from soil flushing solutions. Journal of Hazardous Materials 103: 153-168.
34. Ortega FS, Sepulveda P, Innocentini MDM, Pandolfelli VC (2001) Surfactants: A Necessity for Producing Porous Ceramics. American Ceramic Society Bulletin 80: 37-42.
35. Zhou W, Yang J, Lou L, Zhu L (2011) Solubilization properties of polycyclic aromatic hydrocarbons by saponin, a plant-derived biosurfactant. Environmental Pollution 159: 1198-1204.
36. Hong KJ, Choi YK, Tokunaga S, Ishigami Y, Kajiuchi T (1998) Removal of cadmium and lead from soil using aescin as a biosurfactant. Journal of Surfactants and Detergents 1: 247-250.
37. Kommalapati RR, Roy D (1996) Bioenhancement of soil microorganisms in natural surfactant solutions: I. Aerobic. Journal of Environment Science and Health, Part A Environmental Science 31: 1951-1964.
38. Kommalapati RR, Roy D (1997) Bioenhancement of soil microorganisms in natural surfactant solutions. II. Anaerobic. Journal of Environment Science and Health, Part A Environmental Science 32: 835-847.
39. Mukhopadhyay S, Hashim MA, Sahu JN, Yusoff I, Gupta BS (2013) Comparison of a plant based natural surfactant with SDS for washing of As(V) from Fe rich soil. Journal of Environmental Sciences 25: 2247-2256.
40. Mulligan CN, Yong RN, Gibbs BF (2001) Surfactant-enhanced remediation of contaminated soil: a review. Engineering Geology 60: 371-380.